


PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 03114/PCT-sr	FOR FURTHER ACTION		See Form PCT/PEA/416
International application No. PCT/EP2004/006809	International filing date (<i>day/month/year</i>) 17.06.2004	Priority date (<i>day/month/year</i>) 25.06.2003	
International Patent Classification (IPC) or national classification and IPC B09B3/00, B01J3/00			
Applicant CESI CENTRO ELETTROTECNICO SPERIMENTALE ...			
1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of 10 sheets, including this cover sheet. 3. This report is also accompanied by ANNEXES, comprising: a. <input checked="" type="checkbox"/> <i>sent to the applicant and to the International Bureau</i> a total of 8 sheets, as follows: <input checked="" type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions). <input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box. b. <input type="checkbox"/> (<i>sent to the International Bureau only</i>) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).			
4. This report contains indications relating to the following items: <input checked="" type="checkbox"/> Box No. I Basis of the opinion <input type="checkbox"/> Box No. II Priority <input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability <input type="checkbox"/> Box No. IV Lack of unity of invention <input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement <input type="checkbox"/> Box No. VI Certain documents cited <input type="checkbox"/> Box No. VII Certain defects in the international application <input checked="" type="checkbox"/> Box No. VIII Certain observations on the international application			
Date of submission of the demand 08.04.2005		Date of completion of this report 15.06.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016		Authorized Officer van der Zee, W Telephone No. +31 70 340-2797	



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International application No.
PCT/EP2004/006809

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
 - ☐ This report is based on translations from the original language into the following language, which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages

1, 6-13	as originally filed
2, 3, 4, 4a, 5	received on 22.04.2005 with letter of 15.04.2005

Claims, Numbers

2, 4-11, 13-21	as originally filed
1, 3, 12	received on 22.04.2005 with letter of 15.04.2005

Drawings, Sheets

1/7-7/7	as originally filed
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- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
 - ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
 4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
 - ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-21
	No: Claims	
Inventive step (IS)	Yes: Claims	1-21
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-21
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

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Re Item I

Basis of the report

The examination is carried out on the following application documents:

Description, pages:	1, 6-13	as originally filed,
Description, pages:	2, 3, 4, 4a, 5	as filed with letter of 15.04.2005, received 22.04.2005,
Claims, No:	2, 4-11, 13-21	as originally filed,
Claims, No.	1, 3, 12	as filed with letter of 15.04.2005, received 22.04.2005,
Drawings, sheets:	1/7-7/7	as originally filed.

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Reference is made to the following documents:

- D1: US-A-5562585 (GODESBERG) 8 October 1996 (1996-10-08)
- D2: PATENT ABSTRACTS OF JAPAN vol. 2003, no. 02, 5 February 2003 (2003-02-05) & JP 2002301446 A (ADVANTEST CORP), 15 October 2002 (2002-10-15)
- D3: US-A1-2003/0154590 (WATANABE), 21 August 2003 (21.08.2003)
- D4: EP-A-0905090 (GENERAL ATOMICS) 31 March 1999 (1999-03-31)
- D5: DE-A-19509710 (VEAG VEREINIGTE ENERGIEWERKE AG), 12 September 1996 (1996-09-12)

2. The following is stated under reference to Box VIII of this International Preliminary

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Report on Patentability, whereby it is to be noted that unclear features cannot be employed for assessing novelty or inventive step.

2.1 The document D1 is regarded as being the closest prior art to the subject-matter of claim 1 and discloses (the references in parentheses applying to this document) a process for the hydrothermal treatment of asbestos and/or materials containing asbestos in a heated and pressurized fluid, wherein in succession it provides for the following steps (see the abstract, column 1, lines 7-29 and column 1, line 60 - column 3, line 58):

- withdrawal of a fluid from a source (column 2, lines 1-4 and column 3, lines 20-23);
- transformation of the fluid into a heated and pressurized state (column 2, lines 41-45);
- reaction of the heated and pressurized fluid with asbestos and/or with the material containing asbestos in an environment by means of a hydrolysis process (column 1, lines 7-12 and column 2, lines 45-56).

The subject-matter of claim 1 therefore differs from this known process in that the process is performed using supercritical water as the heated and pressurized fluid and further comprises the following steps:

- withdrawal of water from a tank;
- transformation of the water in supercritical water;
- cooling of the waste water;
- filtering of the waste water;
- collection of the waste water in a tank.

The subject-matter of claim 1 is therefore novel and claim 1 meets the requirements of Article 33(2) PCT.

The objective problem underlying claim 1 is to provide for a process that allows the neutralising of asbestos and/or materials containing asbestos and eliminates the problems associated with the penetration process of known treatment fluids, cf. page 4, lines 28-29 and page 6, lines 6-9.

The solution in accordance with claim 1 is, that the process is performed using supercritical water as the heated and pressurized fluid and further comprises the following steps:

- withdrawal of water from a tank;
- transformation of the water in supercritical water;
- cooling of the waste water;
- filtering of the waste water;
- collection of the waste water in a tank.

Although D2 discloses a process using supercritical water as a reagent fluid, and further comprising the following steps:

- withdrawal of water from a source;
- transformation of the water in supercritical water;
- separating solids from the waste water;
- collection of the waste water in a tank,

cf. the abstract and the figures (see also the passages cited in the International Search Report with regard to the document D3, corresponding to D2 but published between the priority and filing dates of the present application), the combination of the further features of claim 1 is not disclosed by any of the cited prior art documents.

The skilled person is not hinted at the further combination of the withdrawal of water from a tank, cooling of the waste water and filtering of the waste water with the features of D1 and D2 in order to solve the objective underlying problem.

The subject-matter of claim 1 thus involves an inventive step and meets the requirements of Article 33(3) PCT.

- 2.2 Claims 2-11 are all truly dependent claims and also meet the requirements of Article 33(1) to 33(5) PCT.
- 2.3 The document D4 is regarded as being the closest prior art to the subject-matter of claim 12 and discloses (the references in parentheses applying to this document) a plant suitable for the treatment of asbestos and/or materials containing asbestos (see the abstract, paragraphs 0001-0008, 0011-0012, 0022-0026, 0038-0040 and the figures), comprising a water tank (38), a withdrawal pump (42, 44) associated to said tank (38), a furnace (50) containing a serpentine coil fed by said withdrawal pump (42, 44) for the transformation of the water into supercritical water and a reactor (12)

for the reaction of the supercritical water with asbestos and/or with the material containing asbestos (page 5, lines 20-22), heat exchange means (96) for cooling the waste water of said reactor (12), and collection means of the cooled waste water. The subject-matter of claim **12** therefore differs from this known plant in that it comprises means for filtering the water positioned at the output of said exchange means, and an adjustment valve inserted downstream from said heat exchange means, said collection means being located at the output of said filtering means.

The subject-matter of claim **12** is therefore novel and claim **12** meets the requirements of Article 33(2) PCT.

The objective problem underlying claim **12** is to remove any solid materials present (asbestos or asbestos-containing waste) carried along and collect the treated water when the reaction has finished, cf. page 10, lines 24-29.

The solution in accordance with claim **12** is, that the plant comprises means for filtering the water positioned at the output of said exchange means, and an adjustment valve inserted downstream from said heat exchange means, said collection means being located at the output of said filtering means.

Although means for filtering the water positioned at the output of heat exchange means are known from D5, cf. column 2, lines 6-7 and the figure, D5 does not disclose an adjustment valve inserted downstream from said heat exchange means, and collection means being located at the output of said filtering means.

The combination of the further features of claim **12** is not disclosed by any of the cited prior art documents.

The skilled person is not hinted at the further combination of an adjustment valve inserted downstream from said heat exchange means, and collection means being located at the output of said filtering means with the features of D4 and D5 in order to solve the objective underlying problem.

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The subject-matter of claim **12** thus involves an inventive step and claim **12** meets the requirements of Article 33(3) PCT.

- 2.4 Claims **13-21** are all truly dependent claims and also meet the requirements of Article 33(1) to 33(5) PCT.

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Re Item VIII

Certain observations on the international application

With regard to Article 6 PCT, the following is remarked:

1. Independent claim 1 is not in the correct two-part form in accordance with Rule 6.3(b) PCT.

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applications because of its special characteristics such as low cost, flexibility, sound absorption, and resistance to fire, heat and chemical etching. Among the applications of greater significance we can mention: building materials, (the known "EternitTH" contains 15% asbestos in the chrysotile form), the materials used as insulation in railway carriages and in ships, covering for water ducts and air conditioning ducts, anti-friction materials in the linings of brakes in automobiles and railway cars, the yarns for fabrics made for protective garments against fire.

With the Italian regulations the waste materials containing asbestos are classified as toxic-poisonous and the law that prohibits its extraction and import dates back to 1992. At national level their amount is estimated at not less than 15 million tons as asbestos has been generally used together with another material.

Currently there is particular interest in the operations and procedures finalised to recuperation and/or elimination of the asbestos and of the products that contain it. The recuperation interventions, that provide for the removal as well as the discarding of any product containing asbestos that has lost its use designation, that has been abandoned or is scheduled to be abandoned, produce Asbestos-Containing Waste (ACW), that contains a variable quantity of asbestos in the interval (10 - 100)% on weighted base.

A problem that is common to the recuperation and/or neutralising processes of the ACW materials is that associated to the efficiency of transforming the asbestos in inert products that are not dangerous, that is in materials that no longer can be assimilated to fibres that can be breathed in. In fact, for the purpose of evaluating the fibrous asbestos, whose danger is also linked to the dispersion in air, any elongated thready or needle-like solid object is intended with a length equal to or greater than 5 μm , diameter less than 3 μm and with a length/diameter ratio equal to or greater than 3.

The diameter of a fibre takes on basic importance for the capability of it being breathed in, while the length is not very significant as it is very

difficult to breath in the fibres which are longer than 200 μm while the short fibres are eliminated by the clearance of the macrophages.

A recent provision of Italian law (13/03/03) decrees that:

• the waste of asbestos or of materials containing asbestos have to be collected in a dump for dangerous waste, specifically or fitted with a specific cell, where thus it undergoes a process of encapsulation in the site, (that is in the cell of the waste dump).

• if the ACW materials have been submitted to treatment processes, such as: stabilization, encapsulation, embedding, or chemical-physical-thermal treatment, the decree provides for them to be collected in a dump for non-dangerous waste.

Among the main processes known for the treatment of the ACW materials, only the chemical-physical technologies (Yoshiro et al., U.S. Patent 3,941,184; Block, U.S. Patent 5,753,031; U.S. Patent 5,753,032; U.S. Patent 5,753,033; U.S. Patent 5,753,034; U.S. Patent 5,753,035; and Block et al., U.S. Patent 5,743,841) and thermal technologies (Aspireco, European patent n. 0344563; Italian patent n. 20799-M/88) tend to eliminate the potential risk by transforming asbestos in a non-fibrous and non-toxic crystalline phase.

Because of the high costs, the dump is the most common removal process, even though it is less effective as it does not eliminate the asbestos problem, seeing its potential danger remains unaltered.

Over recent years, methods for transforming thready asbestos have been proposed (chrysotile and amosite) in inert materials (US Patent 5,743,841) by means of neutralising the asbestos by etching at a low temperature and pressure. The procedure is based on ^{an} etching by acids using a mixture of a strong acid and a kind capable of generating fluorine in the system. The acid has the task of demolishing the structure of the asbestos hydrolysing the MgO groups, while the fluorine should etch the "silicate" component of the asbestos structure.

The interest for these treatments lies in the fact that they can be easily applied on site directly on the manufactured articles containing asbestos (for example, tubes covered with asbestos-based insulation, whose percentage is around 12%), and therefore there are no problems in transporting dangerous material.

The disadvantages of these treatment methods can be summed up as follows:

- the use of a dangerous reagent, hydrofluoric acid, that requires suitable measures of prevention and safety to be adopted;
- the transformation takes a long time. In fact, the kinetics of the neutralising process by etching depends on two critical factors:
 1. the velocity of penetration (imbibition) of the watery solution inside the manufactured article containing asbestos;
 2. the wettability characteristics of the manufactured article containing asbestos.

Because of these two critical factors the time needed for neutralising is around days. In fact, as given in Block's patent (U.S. Patent n. 5,743,841) starting from ^{an} acid/chrysotile ratio (cementitious mix with 11.7% content of chrysotile) of 1,5:1, the process is basically completed after two days of treatment; in particular Block shows that from the XRD analyses (X-Ray Diffraction) it results that the residual chrysotile after a day is 0.5%, being reducing to 0.1% after 4 days; the treatment is, substantially, a superficial treatment, because of the problems of penetration of the watery solution inside the porous material to be treated.

[PAGE 4a]
The object of the present invention is to provide a treatment procedure and a relative plant that are economically advantageous and that allow the neutralising of asbestos and/or materials containing asbestos and the elimination of the problems associated with the penetration process (imbibition) using a supercritical and oxidising environment (supercritical water, SCW).

- 4a -

JP 2002301446 discloses a treater for circuit member wherein a multilayer substrate reacts with a supercritical water inside a reaction chamber being a hollow elongated ellipsoid cylinder having a cross section of an elongated ellipse composed of small-curvature and nearly linear central parts and large-curvature ends, so that the central parts of the chamber are suited for the entrance of the flat object such as the substrate. Further, the ends have a large curvature and serve to increase the surface area of the inside of the chamber, so that the chamber can withstand to such a high pressure even if the pressure in the chamber is high.

US 5562585 discloses a process for disposal of asbestos or substances containing it wherein the initial material is converted by very fine grinding together with at least one material OH--ions in water in aqueous suspension into a material having non-fibrous stable mineral phases. In a non-hazardous manner therefore, asbestos is eliminated from the end product to be disposed of or otherwise used.

EP 0905090 discloses a system and method for treatment of a feed material includes a reactor chamber in a reactor vessel. The reactor vessel has a longitudinal axis which is vertically oriented so that gravitational forces act generally in a direction along the axis between a top and a bottom of the vessel. A feed material is introduced by a nozzle into the reactor chamber as a jet stream through the top end of the vessel. This jet stream causes back-mixing in the reactor chamber, contributing to rapid initiation of reaction and general down flow of material through the reactor chamber. The material in the reactor chamber can be quenched to dissolve sticky solids in the effluent before the effluent is discharged from the lower end of the vessel. Further, the reactor vessel can include a plug flow section to carry out additional reaction of the feed material.

In accordance with the present invention this object is achieved by means of a process for the hydrothermal treatment of asbestos and/or materials containing asbestos in supercritical water (Supercritical Water, SCW) characterised in that it provides for the following steps:

- 5 - withdrawal of water from a tank;
- transformation of the water into supercritical water;
- reaction of the supercritical water with asbestos and/or with the material containing asbestos in a suitable environment by means of a hydrolysis process;
- 10 - cooling of the waste water;
- filtering of the waste water;
- collection of the waste water in a tank.

In accordance with the present invention this object is also achieved by means of a plant for the treatment of asbestos and/or materials ~~containing~~ *AS DEFINED IN CLAIM 12.* asbestos characterised in that it comprises a water tank, a withdrawal pump associated with said tank, a furnace containing a serpentine coil fed by said withdrawal pump for the transformation of the water into supercritical water and a reactor for the reaction of the supercritical water with asbestos and/or with the material containing asbestos, heat exchange means for cooling the waste water of said reactor, water filtering means placed at the output of said exchange means and collection means for the cooled and filtered waste water/

The operative conditions are preferably the following:

- $400^{\circ}\text{C} < T < 750^{\circ}\text{C}$;
- 25 • $22.11 \text{ MPa} < P < 28 \text{ MPa}$;
- hydrolysis time < 24 hours.

The environmental, energy and productive advantages that would be obtained with the new hydrothermal treatment of asbestos or of materials containing asbestos in supercritical water are multiple and unquestionable.

30 The hydrothermal process of hydrolysis can represent an economical and

CLAIMS

1. Process for the hydrothermal treatment of asbestos and/or materials containing asbestos in supercritical water (~~Supercritical Water, SCW~~) characterised in that in succession ¹¹they provide⁵ for the following steps:

- 5
- withdrawal (3) of water from a tank (2);
 - transformation (5) of the water in supercritical water;
 - reaction of the supercritical water with asbestos and/or with the material containing asbestos in a ~~suitable~~ environment (8) by means of a hydrolysis process;

- 10
- cooling (14) of the waste water;
 - filtering (15) of the waste water;
 - collection of the waste water in a tank (17).

2. Process according to claim 1, characterised in that said water is distilled.

15 3. Process according to claim 1, characterised in that said water is oxygenated^d.

4. Process according to claim 1, characterised in that it is produced in a confined environment.

20 5. Process according to claim 1, characterised in that it is carried out in continuous modality.

6. Process according to claim 1, characterised in that it is carried out in discontinuous modality.

25 7. Process according to claim 1, characterised in that it is carried out in semi-batch modality, that is with water in continuous modality and solid material in discontinuous modality.

8. Process according to claim 1, characterised in that it is carried out in the following conditions of temperature T, pressure P and hydrolysis time:

- 30
- $400^{\circ}\text{C} < T < 750^{\circ}\text{C}$;
 - $22.11 \text{ MPa} < P < 28 \text{ MPa}$;
 - hydrolysis time < 24 hours.

9. Process according to claim 1, characterised in that, before the reaction with the supercritical water, the asbestos and/or the material containing asbestos is submitted to a wet pretreatment.

5 10. Process according to claim 9, characterised in that said wet pretreatment provides for the breaking up and grinding of the asbestos and/or of the material containing asbestos in the presence of water.

11. Process according to claim 9, characterised in that said pretreatment comes about with additives.

10 12. Plant ^{substantive} for the treatment of asbestos and/or materials containing asbestos ^{IN P} characterised in that it comprises a water tank (2), a withdrawal pump (3) associated to said tank (2), a furnace (4) containing a serpentine coil (5) fed by said withdrawal pump (3) for the transformation of the water in supercritical water and a reactor (8) for the reaction of the supercritical water with asbestos and/or with the material containing asbestos, heat exchange means (14) for cooling the waste water of said reactor (8), ~~and~~ ^{ET COMPRISES} means for filtering (15) the water positioned at the output of said exchange means (14), ^{and} ~~and~~ collection means (17) of the cooled ~~and filtered~~ waste water, ^{AND []}

15 13. Plant according to claim 12, characterised in that said water is distilled.

20 14. Plant according to claim 12, characterised in that said water is oxygenated.

15. Plant according to claim 12, characterised in that it is in a confined environment.

25 16. Plant according to claim 12, characterised in that the reactor (8) is made to function with the following values of temperature T, of pressure P and hydrolysis time:

- $400^{\circ}\text{C} < T < 750^{\circ}\text{C}$;
- $22.11 \text{ MPa} < P < 28 \text{ MPa}$;
- hydrolysis time < 24 hours.

30 17. Plant according to claim 12, characterised in that the furnace (4) is

electric.

18. Plant according to claim 12, characterised in that said furnace (4) is a fluidised bed.

5 19. Plant according to claim 12, characterised in that said reactor (8) is a water storage tank.

20. Plant according to claim 12, characterised in that said reactor (8) can be extracted from the furnace (4).

21. Plant according to claim 12, characterised in that said exchangers (14) have a serpentine coil.

10 ~~22. Plant according to claim 12, characterised in that it comprises~~ (an adjustment valve (16) inserted downstream from said heat exchange means (14), SAID COLLECTION MEANS (17) BEING LOCATED AT THE OUTPUT OF SAID FILTERING MEANS (15)).